# Carbon Supported Polyaniline
# as Anode Catalyst:
# Pathway to Platinum-Free Fuel Cells

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## Abstract

The effectiveness of carbon supported polyaniline as anode catalyst in a fuel cell (FC) with direct formic acid electrooxidation is experimentally demonstrated. A prototype FC with such a platinum-free composite anode exhibited a maximum room-temperature specific power of about 5 $mW/cm^2$

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1. The main advantage of fuel cells (FC) employing liquid organic fuels as compared to those using hydrogen is the simplicity of storage and recharging. Among the FC with liquid fuels, the most thoroughly studied are FC with direct methanol electrooxidation (DMFC) [1]. The other potential liquid organic fuels include formic acid. In FC employing direct formic acid electrooxidation (DFAFC) [2], a somewhat lower energy capacity (as compared

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1

to that of DMFC) is compensated by other advantages, including relatively simple reaction nature (and, accordingly, facilitated problem of catalyst selection) and lower extent of fuel crossover through the proton-conducting (nafion) membrane.

As is known, direct electrochemical oxidation of organic fuels on the FC anode leads to the formation of $CO_2$ (complete oxidation). In the case of DFAFC, the process is:

$$HCOOH \quad \rightarrow \quad CO_2 + 2H^+ + 2e^- \tag{1}$$
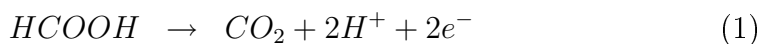
The active evolution of carbon dioxide is a reliable manifestation of this reaction. The process on the cathode consists in the reduction of molecular oxygen $O_2$ with the formation of water $H_2O$ :

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \quad \rightarrow \quad H_2O \tag{2}$$
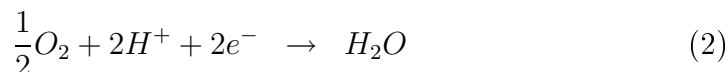
It should be noted that cathodic reaction (2) is common to all FC with proton-conducting membranes, which use oxygen as the oxidizer.

The main problems inherent in all FC with direct electrochemical oxidation of organic fuels are the following:

(a) The output power yield is limited by the rate of anodic reaction and usually varies at room temperature within 5—20 $mW/cm^2$ [3–5].

(b) The fuel crossover through a nafion membrane to cathode and its oxidation on the FC cathode surface is equivalent to an opposite emf [4, 6], that is, to a decrease in output power and in the FC efficiency.

(c) Some organic fuels produce degradation of nafion membrane in the course of FC operation.

The anode and cathode of FCs are electrodes with catalytic coatings, which are usually based on platinum (Pt). The limited resource of this metal on the Earth stimulates the interest in creating nonplatinum catalysts.

For cathodic reaction (2), catalysts containing no metallic platinum have been developed based on macrocyclic complexes (see [3, 7] and references therein), biological materials [8], and transition metal compounds [3, 6, 7]. It was also reported that polyaniline (PANI) exhibited catalytic activity in the reaction of oxygen reduction in air–metal cells [9]. All these systems exhibit a lower catalytic activity than platinum, but their development and practical use nevertheless good have prospects.

2

In recent years, FC units have been developed with extensive use of conducting polymers (synthetic metals) such as PANI, polypyrrole, and polythiophene [10–12]. Some data [3, 13] and our previous results [14, 15] indicate that polymers with electron–proton conductivity (such as PANI) can increase the efficacy of platinum group metal catalysts [16].

As for anodic reaction (1), no catalysts free of platinum group metals have yet been reported, although there were communications on the catalytic activity of PANI in the reactions of anodic oxidation of hydrogen [17], methanol [18], and ascorbic acid [19]. As is known, PANI combines a high level of electron (hole) conductivity ($1 - 10$ S/cm [11, 12]) with proton conductivity (up to $10^{-2}$ S/cm) [15, 20, 21]. The mixed conductivity type of this polymer is of key importance in electrochemical processes involving simultaneous transport of both protons and electrons. It should also be noted that PANI has a variable structure; this polymer contains benzoid and quinoid fragments linked via nitrogen atoms occurring in various oxidation and protonation states. The ratio of the fragments of various types can change in a reversible manner depending at least on two parameters of the reaction medium: oxidation potential and acidity [11]. This circumstance provides broad possibilities for controlled modification of the properties of PANI.

2. This preprint reports the process of electrochemical oxidation of formic acid in an FC with the anode made of a carbon material coated with a nanolayer (100 nm) of PANI. PANI in an emeraldine form was obtained via aniline oxidation with ammonium peroxydisulfate immediately on the surface of fibers of a porous carbon material [22]. The resulting PANI was strongly adsorbed on the carbon substrate. The polymer nanolayer encapsulated carbon fibers in the entire volume of the porous carbon matrix, so that the total weight fraction of PANI in the resulting composite reached 20%.

The electro- chemical cell schematically depicted in Fig. 1. In order to study the anodic reaction, we used a cathode half–MEA (membrane–electrode assembly) [23] comprising a Nafion 117 membrane with the standard DMFC cathode containing $4$mg/cm$^2$ of platinum. The cathode operated in air under natural convection conditions.

The anode was made of Torray TGPH-060 carbon cardboard covered with PANI nanolayer as described above. The cardboard was pressed against the nafion membrane with a thicker cardboard (free of PANI coating), which simultaneously served as electrode and gasdiffusion medium. The fuel was a 5% solution of formic acid (HCOOH) in a 0.5M aqueous $H_2SO_4$ solution. Since the experiments were performed with a fuel possessing ionic conduc-

tivity, the problem of contact quality in the anodic region was not so important, since protons could readily pass from one medium to another via the ion-containing fuel.

Figure 2 shows the experimental loading characteristics measured using a prototype FC describe above. Plots of the FC output voltage versus current density in the membrane had the typical form, beginning at about 0.7V (at a nearly zero current density) and rapidly decaying at current densities below $5 \ mA/cm^2$ . Using the subsequent less steep decrease, the internal resistance of the FC prototype was estimated at about 10 $\Omega cm^2$. The maximum specific output power reached in our experiments at room temperature was about 5 $mW/cm^2$ . This value corresponds to the output power of the typical DMFCs operating at room temperature (20C) [3, 4]. In the region of high current densities (10–40 $mA/cm^2$), the curves were poorly reproduced in different experimental runs.

As was noted above, the active gas evolution on the FC anode operating on formic acid fuel is a reliable criterion for reaction (1) to actually take place. Indeed, when the FC was connected to a low-ohmic load and a relatively large current passed through the cell, intensive evolution of $CO_2$ bubbles (Fig. 3) was observed. The volume of liberated gas was measured and compared to the amount of charge transported vie the FC circuit. In this calculation, we assumed that the oxidation of the HCOOH molecule yields a charge of $2 \times 1.6 \cdot 10^{-19} C$. The volume of $CO_2$ calculated for the transferred charge was 1.8 times the volume evolved in the experiment. The reason for so large a discrepancy is still unclear. One possible explanation is offered by the following mechanism: a fraction of current could be, in principle, related to the additional oxidation of PANI with the formation of pernigraniline. However, calculations showed that an additional charge provided by complete oxidation of PANI present on the anode was two orders of magnitude lower than the total charge transported in the experiment.

Thus, the electrochemical oxidation of formic acid is the only process that can be responsible for the liberation of energy in the prototype FC studied. Moreover, if the observed current were related to PANI oxidation, the output current would unavoidably drop from one run to another, which was not observed in our experiments.

The experiments showed no systematic decrease in the output power during the first two days. In the family of loading curves presented in Fig. 2, the curves corresponding to the maximum current and density were obtained in the last experimental run of the series. The current and output power

exhibited a reversible decrease as a result of the fuel consumption in the FC and were restored on the initial level upon adding a new portion of the fuel. However, the experiments performed in the following days showed a decrease in the current and approximately proportional decrease in the FC open-circuit voltage (down to 0.4V), and even to a lower level in the subsequent week. We explain this behavior by the diffusion (crossover) of formic acid in the membrane, which results in the appearance of fuel on the oxidizer side and is equivalent to the opposite emf operation [4, 6]; an additional detrimental factor is degradation of the nafion membrane surface in contact with formic acid.

It is necessary to emphasize the stability of results. The electrochemical oxidation of formic acid is not characteristic of the given type of carbon material. Specific output power on a level of $3 - 5 mW/cm^2$ was also obtained in prototype FCs where PANI was supported (instead of Torray TGPH-060) on carbon materials of the Kinol ACC-10-20 or Busofit T-1-55 types.

Thus, the results of our experiments convincingly demonstrated the catalytic activity of PANI in the anodic reaction of formic acid oxidation.

3. We can only suggest some notions concerning the nature of the catalytic activity of PANI. One possible mechanism is the reduction of PANI from the emeraldine to leuco-emeraldine form, which is accompanied by the oxidation of formic acid and is followed by leuco-emeraldine oxidation to emeraldine and electron transfer to the anode. We believe that the redox transition of PANI from the emeraldine form to a lower oxidation state (leuco-emeraldine) mediates in the electron transfer and accelerates the oxidation of formic acid.

Another special question concerns the possible role of the carbon-PANI interface in the enhancement of the catalytic activity. We suggest that, since PANI is a p-type conductor [24] and carbon materials possess metallic conductivity, this interface features a potential barrier of the Schottky type. Since PANI is a medium permeable to liquids (in this case, to formic acid), HCOOH molecules occur in a strong electric field near the proton-conducting membrane and the field induces their polarization, which can in principle lead to a decrease in the dissociation energy. The close phenomenon of the polarization and subsequent ionization of shallow impurity states in the electric field is well known in semiconductor physics [25].

4. Thus, we have experimentally demonstrated that carbon supported PANI exhibits high catalytic activity in the reaction of anodic oxidation (1) of formic acid in fuel cells of the DFAFC type. This activity was observed

5

in a working prototype FC with nonplatinum composite anode of the carbon supported PANI type, which ensured a stable specific output power of about $5 \ mW/cm^2$ over a long period of time. In combination with published data on the nonplatinum catalysts for the cathodic reaction, these results open the way to the creation of FCs entirely free of platinum catalysts, which is the aim of our further investigations [26].

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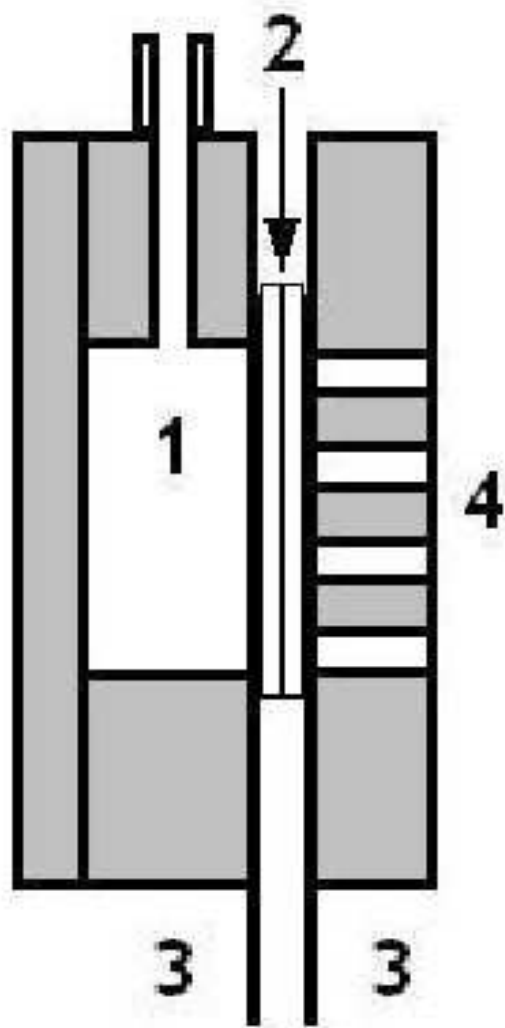
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Figure 1: Schematic diagram of the electrochemical cell involving a cathode half-MEA: (1) liquid fuel container; (2) membrane–electrode assembly (see the text for details); (3) plate electrodes with holes; (4) case with air channels. Spacers and screws are not shown.
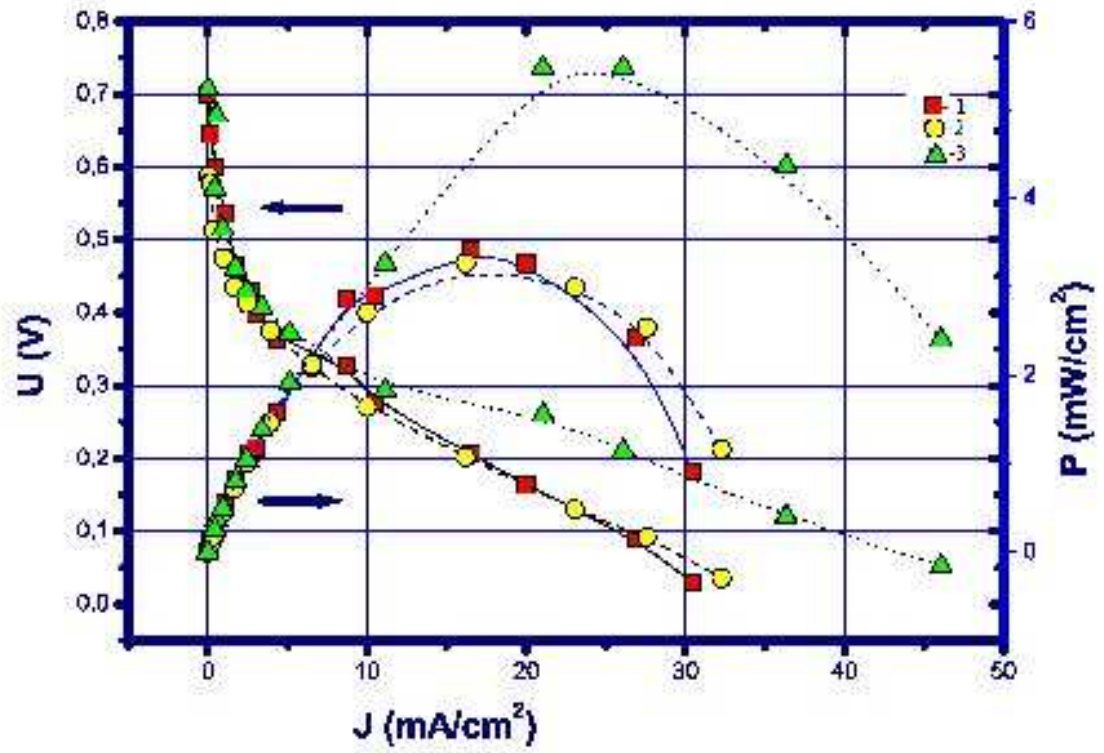
Figure 2: Plots of voltage U (left scale) and specific power (right scale) versus current density measured in a prototype FC. Curves 1–3 refer to three sequential experimental runs performed with a 10-min time interval.

Figure 3: $CO_2$ evolution on the anode of operating FC.